

CHAPTER IV

RESULTS AND DISCUSSION



4.1 Morphology

The starch-based composite foams were prepared by baking process. According to Shogren *et al.* (1998a) who studied the structure and morphology of baked starch foams, the process of foaming a starch batter inside a heated, closed mold can be divided into several steps. First, the temperature of the starch-water mixture inside the mold rises above the starch gelatinization temperature or to the boiling point. Next, the starch gelatinizes and becomes a thick paste at which point the steam trapped in the paste expands causing the paste to fill the mold and begin to exit the vents around the edge of the mold. As this happens, a small amount of pressure (~1 bar) builds inside the mold thus increasing the internal temperature and accelerating the exit of steam and excess starch paste from the mold. During the final and longest step, the starch foam gradually dries to 2-4% moisture as water slowly escapes through the vents.

Scanning electron micrograph of starch foams is shown in figure 4.1. (A). Cross-sectional view shows that the foam has dense outer skins with small cells and less dense interiors with large cells. The outer skin is more dense because, being close to the hot mold, the starch paste dries rapidly and therefore cannot expand very extensively. The interior of the foam contains mostly large, open cells due to the large amounts of steam venting outside the mold and consequent cell rupture (Shogren *et al.*, 1998a).

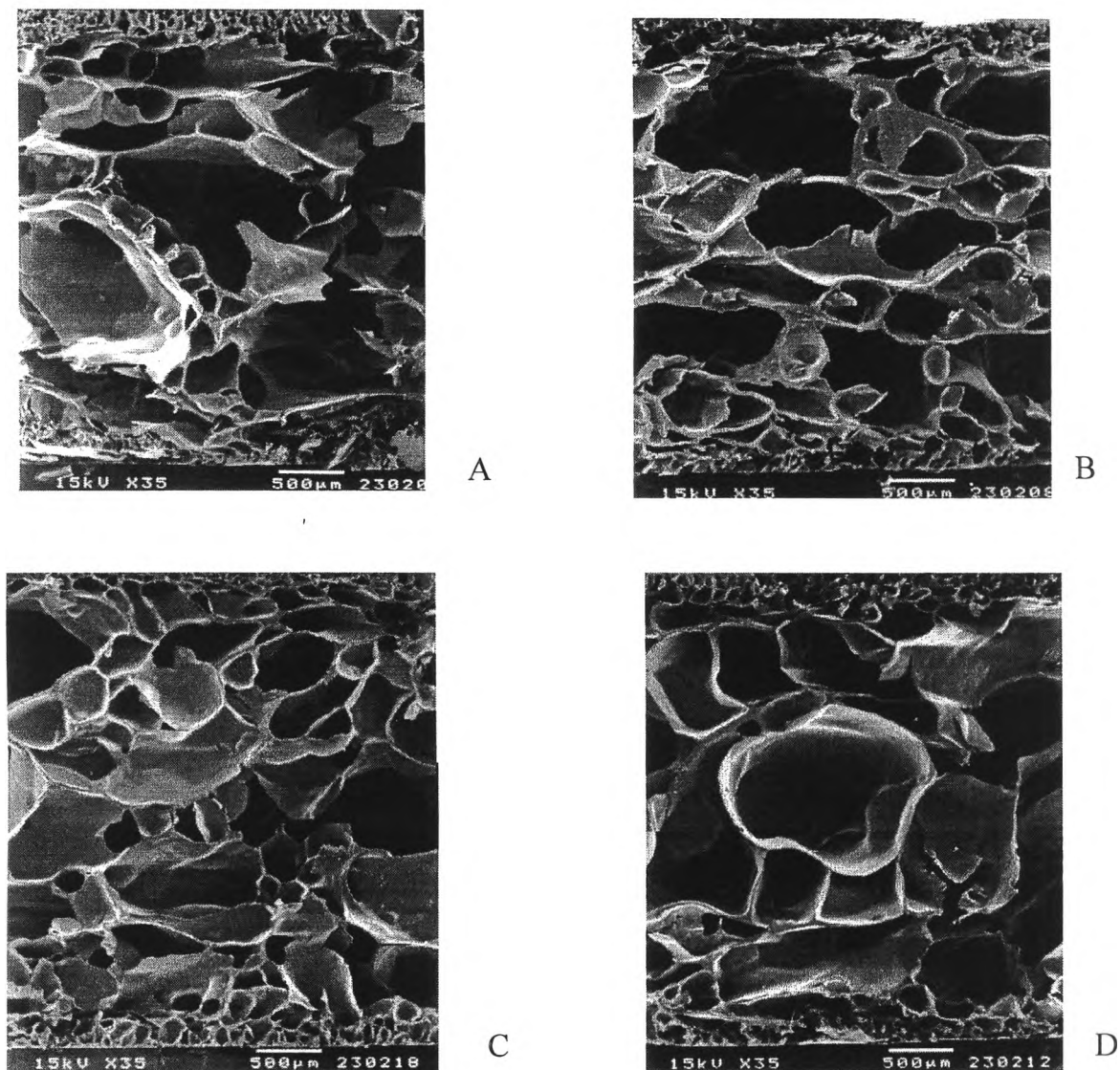


Figure 4.1 Scanning electron micrograph of cross sections of (A) starch foam, (B) starch-30% PVA, (C) starch-30% PLA, and (D) starch- 30% PCL.

Scanning electron micrographs of starch-based composite foams containing PVA, PLA, and PCL are shown in figure 4.1 (B), (C), and (D), respectively. Similar to scanning electron micrograph of starch foam, the foams have dense outer skins with small cells and less dense interiors with large cells. Photomicrographs of starch-based composite foams show their

cell sizes and shapes. Foams containing PCL show a greater number of larger cells.

The densities of starch-based composite foams were also investigated. The density of starch foam was 0.138 g/cm^3 while the densities of starch-30% PVA, starch-30% PLA, and starch-30% PCL was 0.2250, 0.2170, and 0.2042 g/cm^3 , respectively. It was found that the density of foams containing PCL was lower than those of foams containing PVA and PLA.

4.2 Moisture Content

Because of the hydrophilic property of starch, starch-based composite foams have a limited resistance to water absorption and deform upon the exposure to moisture, which makes them unsuitable for some packaging applications. Therefore, it is important to determine the moisture content of these materials. The amount of water adsorbed by starch-based foams greatly influences different properties of starch-based foams, such as their mechanical properties, their mass and their storage stability against microorganisms (Liebenspacher and Weisser, 1989).

There are several factors such as relative humidity, storage time, polymers, and plasticizers that can effect on moisture content of starch-based composite foams. Alexander (2000) who studied the water vapor sorption determination of starch-based porous packaging materials and found that the water content of starch-based foams influenced their mechanical properties. At relative humidities above approximately 85% capillary condensation took place, the water content increased significantly resulting in decreasing of the stability of the starch-based foams and mechanical properties. Moreover, Stenhouse (1997) studied the structure and properties of starch/poly(ethylene-co-vinyl alcohol) blown films and reported that the properties of the films varied with moisture content and therefore with relative humidity. At high moisture content, strength was reduced, while at low moisture content,

flexibility was reduced. Other deficiency was the increasingly brittle nature of the films as a function of storage time

4.2.1 Effect of Relative Humidity

The effect of relative humidity on the moisture content of starch-based composite foams containing PVA, PLA, and PCL at 25°C conditioned for 7 days is shown in figure 4.2. For all formulations, moisture content increases with the increasing of relative humidity. At low relative humidities most water molecules are strongly sorbed and are almost immobilized on polar sorption sites of materials. In this region only monomolecular adsorption layers of water molecules occur. With increasing relative humidity double and multiple layers of water molecules are formed and finally the slope of the curves increases rapidly (Kessler, 1981).

For starch-PVA foams (figure 4.2 (A)), moisture content decreases with increasing amount of PVA. Starch-PLA foams and starch-PCL foams are shown in figure 4.2 (B) and (C), respectively. Similar to starch-PVA foams, moisture contents of starch-PLA foams and starch-PCL foams decrease with increasing amount of PLA and PCL. This is due to hygroscopic property of starch. Starch absorbs moisture more than synthetic polymers. When the polymer content increases, which means starch content decreases, the moisture content decreases.

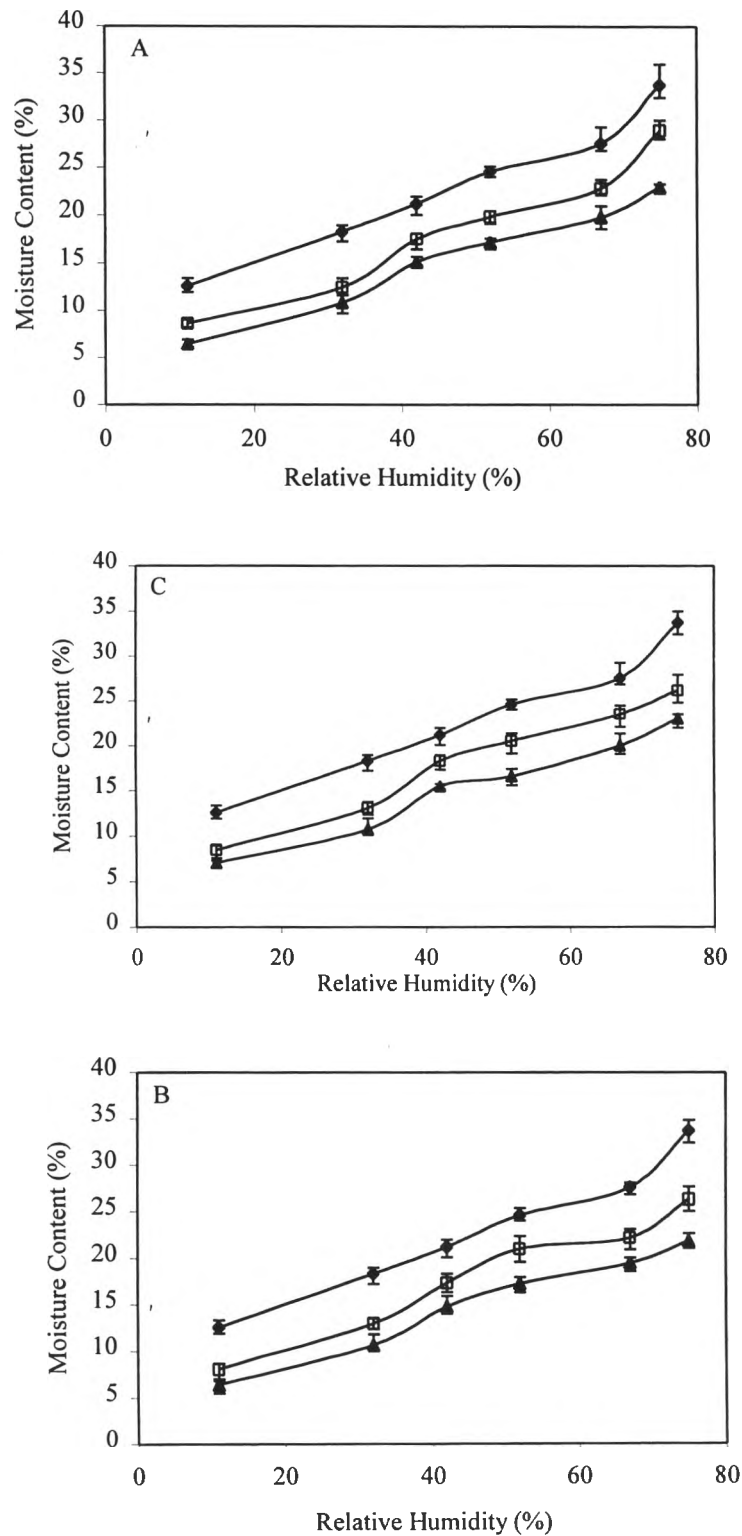


Figure 4.2 Moisture contents of starch-based composite foams as a function of relative humidity at 25°C for 7 days of (A) starch-PVA foams, (B) starch-PLA foams, and (C) starch-PCL foams: (◆) 0% synthetic polymer, (□) 10% synthetic polymer, and (▲) 30% synthetic polymer.

4.2.2 Effect of Storage Time

The effect of storage time on the moisture content of starch-based composite foams containing PVA, PLA, and PCL during keeping at a controlled humidity of 42% RH is shown in figure 4.3. The moisture content increases when storage time at controlled humidity increase for all starch-based composite foams.

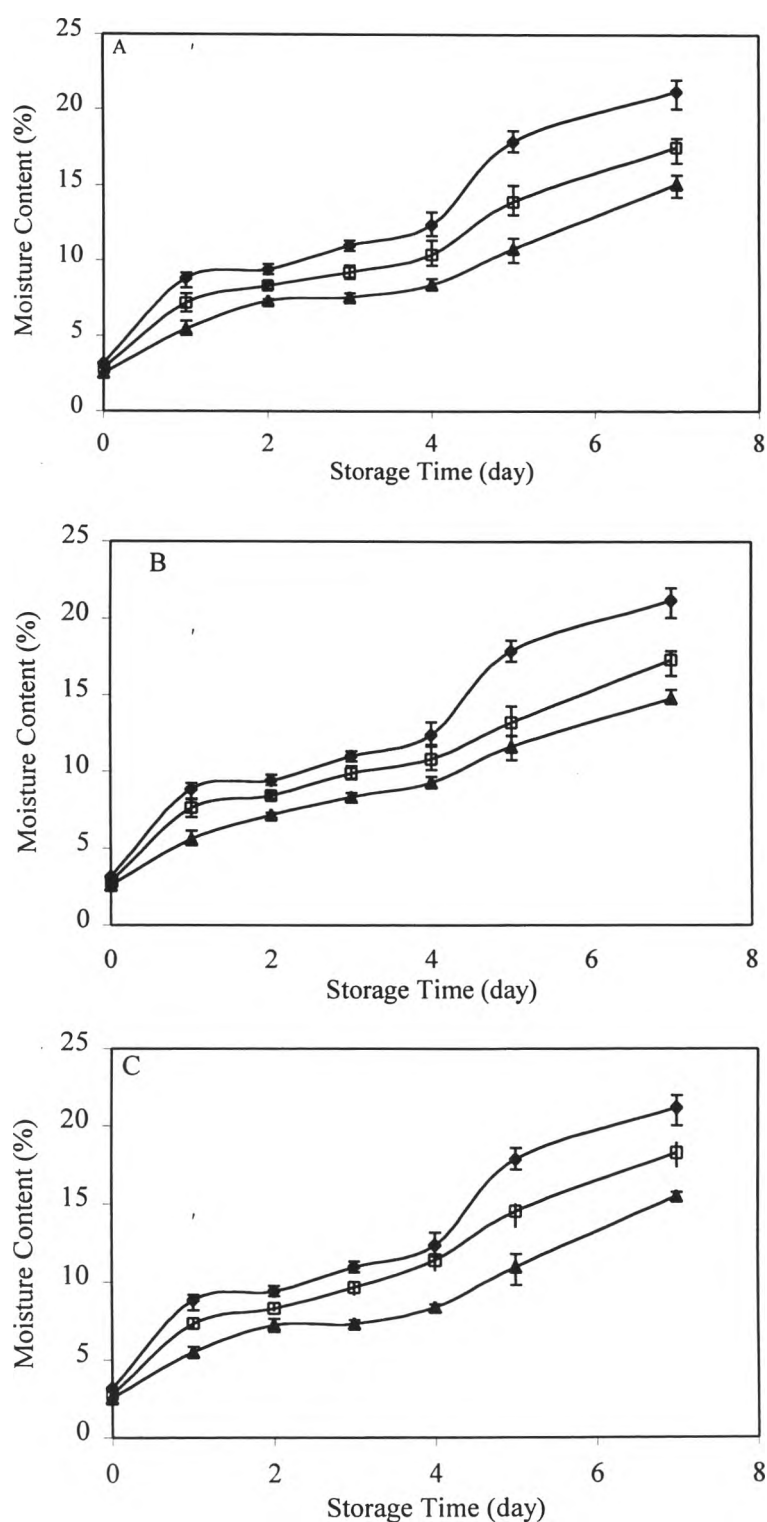


Figure 4.3 Moisture contents of starch-based composite foams as a function of storage time at 42% RH and 25°C of (A) starch-PVA foams, (B) starch-PLA foams, and (C) starch-PCL foams: (◆) 0% synthetic polymer, (□) 10% synthetic polymer, and (▲) 30% synthetic polymer.

4.2.3 Effect of Polymer

The factors that affect the moisture content of the foams considered in this topic were types and amounts of polymers. Lai *et al.* (1991) found that as the PVA content increased, the moisture content of the nylon 4/PVA blended membrane decreased. Similarly, Averous *et al.* (2000) reported blending of thermoplastic starch with PCL could increase the water-resistant of the blend. Fang and Hanna (2000) found that foams containing PLA had improved water resistance values as compared with commercially available starch foam containing 97% starch.

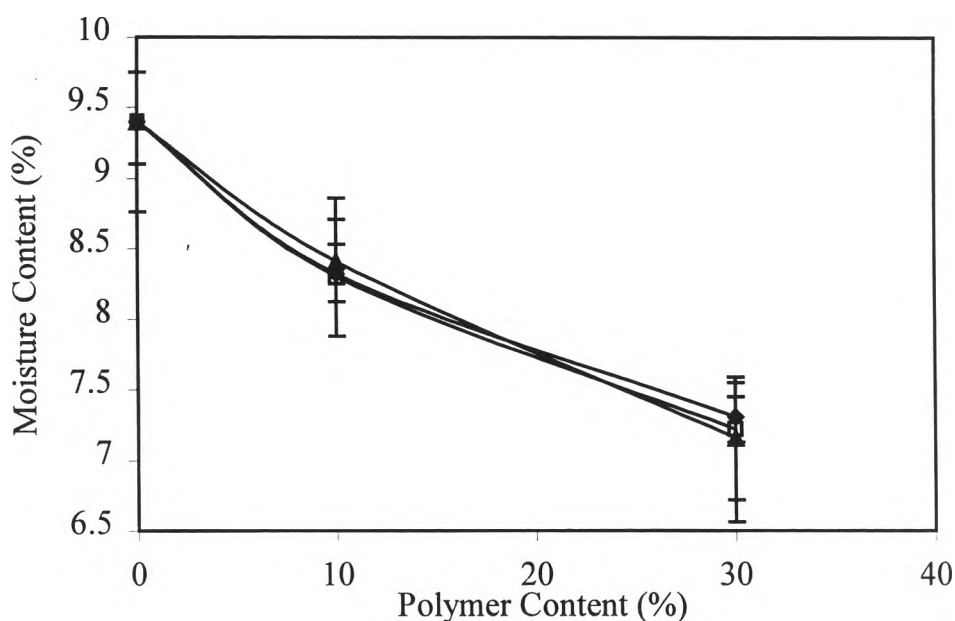


Figure 4.4 Moisture contents of starch-based composite foams at 42% RH for 2 days of (◆) starch-PVA foams, (□) starch-PLA foams, and (▲) starch-PCL foams.

Figure 4.4 shows the moisture content of starch-based composite foams as a function of polymer content. It was found that the moisture content decreases with increasing polymer content. Moreover, it does not show much

different in decreasing of moisture content for each type of composite foams as compared to starch foam.

4.2.4 Effect of plasticizers

Various plasticizers have been used by several researchers in order to make starch more flexible. Shogren (1992) reported that using urea mixed with various glycols could increase the toughness (elongation at break) of gelatinized starch to a greater extent than using either plasticizer alone. Van Soest and Knooren (1997) who studied the effect of glycerol and water content on the properties of starch plastic sheets during aging reported that difference in plasticizer content can change the water content and mechanical properties of starch plastic sheets during aging

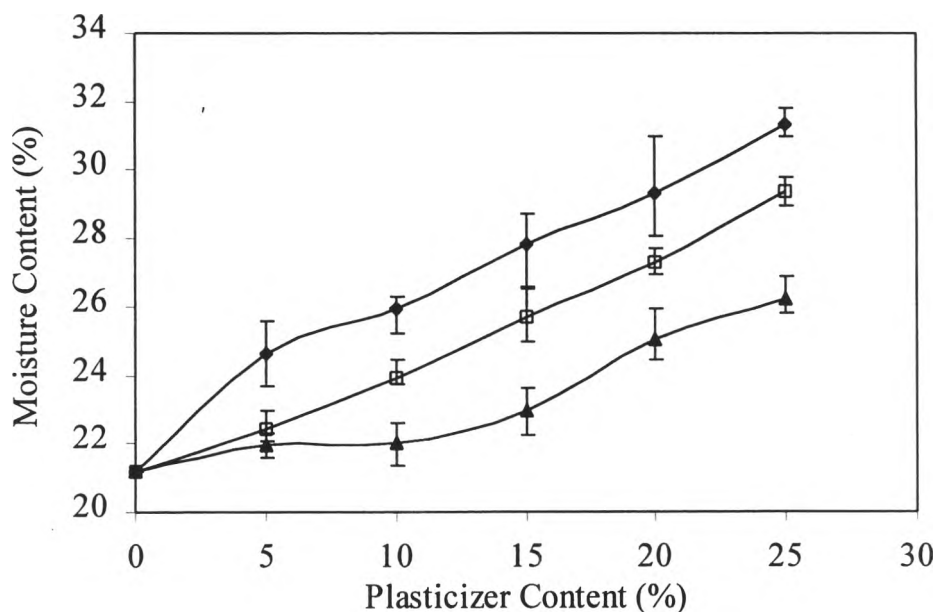


Figure 4.5 Moisture contents of starch-based composite foams at 42% RH for 2 days of (◆) glycerol, (□) urea, and (▲) ammonium chloride.

The moisture content of starch foams containing glycerol, urea, and ammonium chloride conditioned at 42% RH for 7 days is shown in figure 4.5. The starch foams containing glycerol have a higher moisture content than

those containing urea and ammonium chloride. All samples showed increase in moisture content with increasing amounts of plasticizers.

4.3 Mechanical Properties

Foams exhibit physical and mechanical properties related to their compositions and storage conditions such as relative humidity and storage time (Roberta *et al.*, 1998). For composition, Zhiqiang *et al.* (1999) found that the addition of PVA improve mechanical strength, weatherability, and water resistance of the starch/PVA membrane. Schroeter and Hobelsberger (1992) studied on the effect of PCL content on the mechanical properties of composites of granular starch and PCL. They reported that the starch/PCL composites showed a steady decreased in relative tensile strength with decreasing PCL content. Avella *et al.* (2000) who studied the preparation and characterisation of compositibised polycaprolactone/starch composite found that strength at yield decreased with decreasing PCL content. Fang and Hanna (2000) reported that the PLA content had some influences on the mechanical properties of starch-PLA foams. As the PLA content increased, the values of compressibility changed slightly; the spring indices increased from 80.8 to 90.4% as the PLA content increased from 10 to 40%. Therefore, increasing the PLA content made the foam more elastic. Shogren *et al.* (1998b) found that maximum force of starch-PVA foams depended on relative humidity. At low and high humidities, foams showed low strength while 50% humidity, foams gave the maximum strength. Van Soest and Knooren (1997) reported that the elongation decreased rapidly during the first week while the young modulus and the tensile stress increased. During storage for over 1 week, only slight changes in elongation were observed. The young modulus of the materials showed almost no increase after the first week of storage.

In this study, the effect of relative humidity, storage time, different types of polymers, and plasticizers on tensile and flexural properties of the composite foams were investigated.

4.3.1 Tensile Properties

4.3.1.1 *Effect of Relative Humidity on Tensile Properties*

Tensile properties were measured after conditioning the foams at different relative humidities at 25°C for 7 days. The results are plotted as a function of relative humidity and shown in figure 4.6 and 4.7 for the starch-based composite foams with different types of polymers (PVA, PLA, and PCL).

The tensile strength of starch-based composite foams containing PVA, PLA, and PCL are shown in figure 4.6. The maximum tensile strength was found at approximately 42% RH for all composite foams. Because at low humidities, brittleness and crack formation lead to lower strength, while at high humidities, the plasticizing effect of absorbed water lowers the strength (Shogren *et al.*, 1998a). Moreover, it was found that the addition of polymers improved the tensile strength of starch-based composite foams significantly over simple starch foams.

The percent elongation at break of starch-based composite foam containing PVA, PLA, and PCL are shown in figure 4.7. It was found that elongation at break increased with increasing relative humidity and became constant at relative humidity higher than 42%. The dramatic increase in elongation at break during increasing humidity may be due to the effect of water absorbed in starch phase which increases mobility of starch (Shogren *et al.*, 1998b).



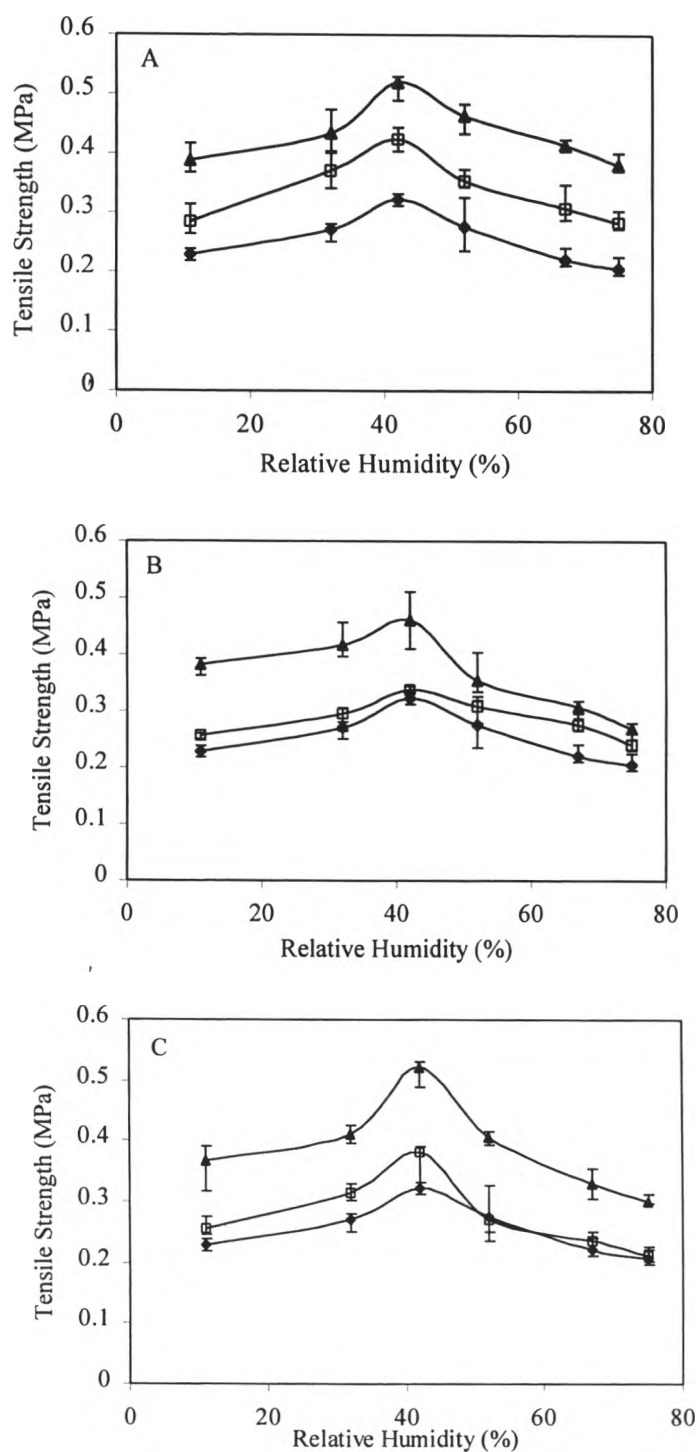


Figure 4.6 Tensile strength of starch-based composite foams as a function of relative humidity at 25°C for 7 days of (A) starch-PVA foams, (B) starch-PLA foams, and (C) starch-PCL foams: (◆) 0% synthetic polymer, (□) 10% synthetic polymer, and (▲) 30% synthetic polymer.

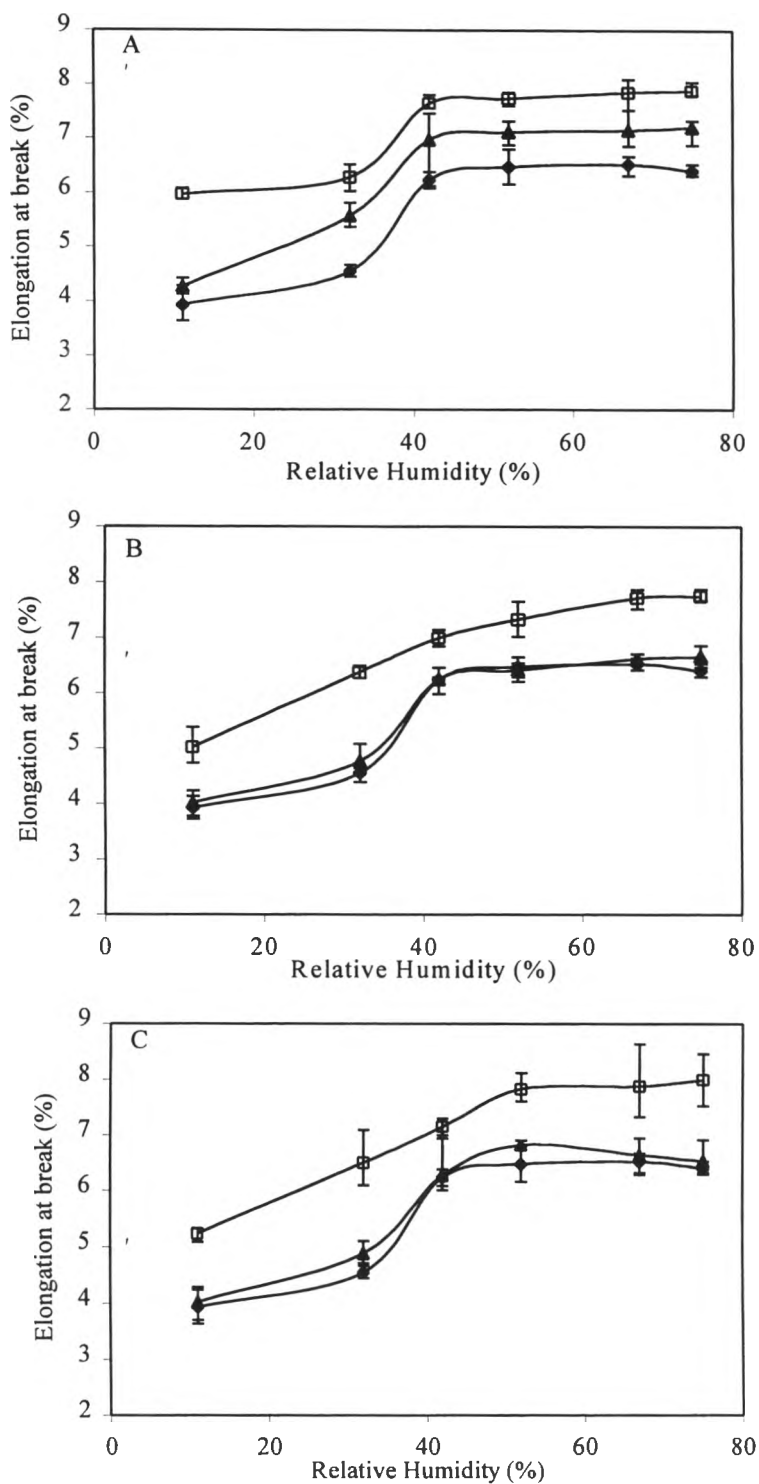


Figure 4.7 Elongation at break of starch-based composite foams as a function of relative humidity at 25°C for 7 days of (A) starch-PVA foams, (B) starch-PLA foams, and (C) starch-PCL foams: (◆) 0% synthetic polymer, (□) 10% synthetic polymer, and (▲) 30% synthetic polymer.

4.3.1.2 Effect of Storage Time on Tensile Properties

Tensile properties were measured after conditioning the foams at constant relative humidity of 42% RH at 25°C for several periods of time. The results are plotted as a function of storage time for the starch-based composite foams containing different types of polymers (PVA, PLA, and PCL).

The effect of storage time on tensile strength of starch-based composite foam containing PVA, PLA, and PCL are shown in figure 4.8. All formulations of starch-based foams have maximum tensile strength at the second day of storage time. It could be due to the plasticizing effect of absorbed moisture at that time. In comparison of 0, 10, and 30% polymers it has been seen that increasing the amount of polymer made the tensile strength of the composite foams increase. In general, PVA, PLA, and PCL have greater tensile strength than that of starch so increasing the amounts of polymers could improve tensile strength of the composite foams (Chang-Hyeon, 1999; Averous, 2000; Fing and Hanna, 2000).

The elongation at break of starch-based composite foams containing PVA, PLA, and PCL are shown in figure 4.9. For all formulations, the elongation at break rises steeply during storage for 4 days. After 4 days, the elongation at break slightly decreases. The increase in elongation of the starch-based composite foams during the first 4 days of storage time may be due to the rapid uptake of moisture content on the starch phase during storage (Stenhouse & Ratto, 1996). In comparison of 0, 10, and 30 % polymer content it has been seen that there is an inverse relationship between the elongation at break and the amounts of polymers. Generally, the elongation of starch foam is less than the synthetic polymers because starch foams are weak and more brittle than PVA, PLA, and PCL (Shogren & Lawton, 1997; Averous, 2000; Fang and Hanna, 2000). Compared composite foams containing between 10 and 30% polymer, the elongation at break of 10% polymer are higher than that

of composite foam containing 30% polymer for all polymers (PVA, PLA, and PCL) because of the hardness of starch foams after adding polymer (Zhiqiang *et al.*, 1999).

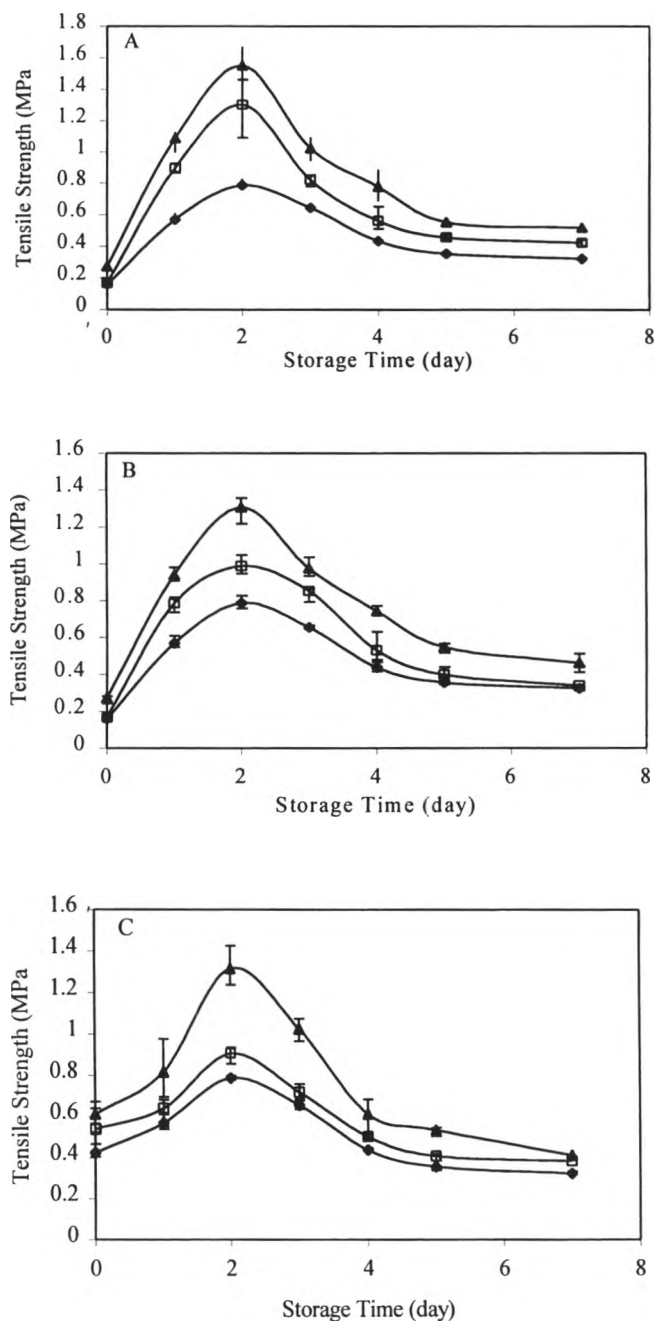


Figure 4.8 Tensile strength of starch-based composite foams as a function of storage time at 42% RH and 25°C of (A) starch-PVA foams, (B) starch-PLA foams, and (C) starch-PCL foams: (◆) 0% synthetic polymer, (□) 10% synthetic polymer, and (▲) 30% synthetic polymer.

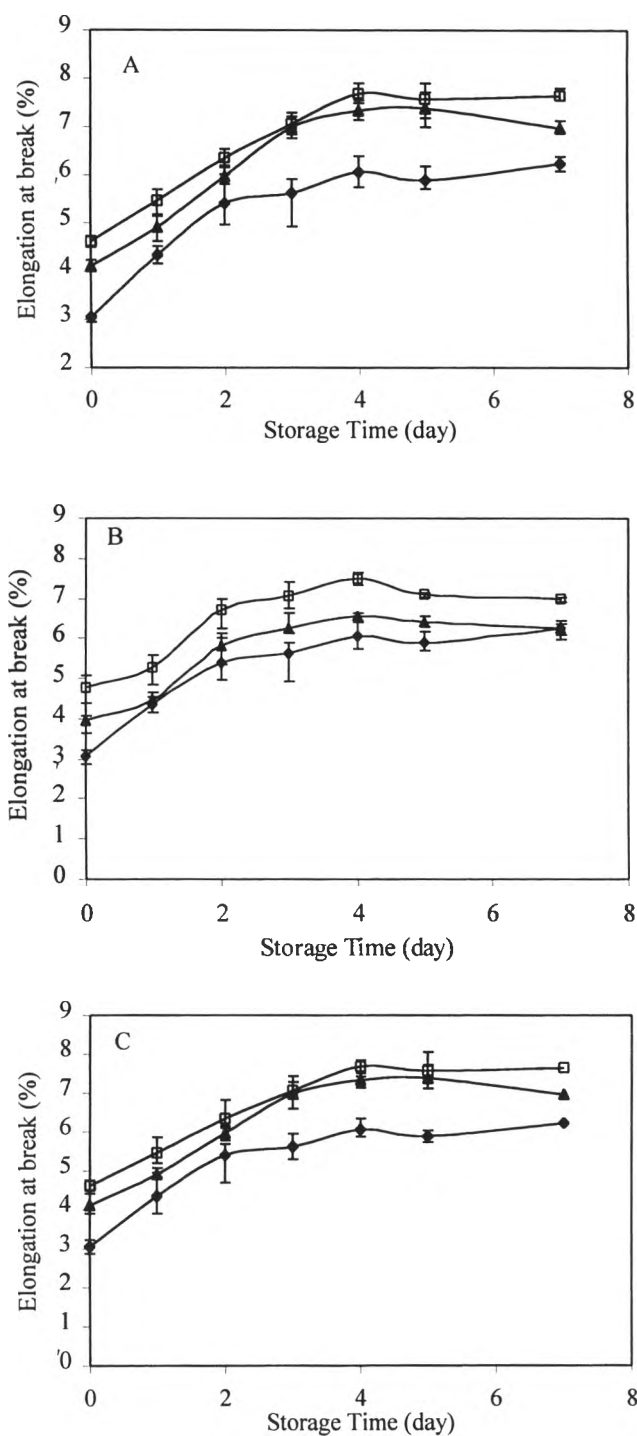


Figure 4.9 Elongation at break of starch-based composite foams as a function of storage time at 42% RH and 25°C of (A) starch-PVA foams, (B) starch-PLA foams, and (C) starch-PCL foams: (♦) 0% synthetic polymer, (□) 10% synthetic polymer, and (▲) 30% synthetic polymer.

4.3.1.3 Effect of Polymer on Tensile Properties

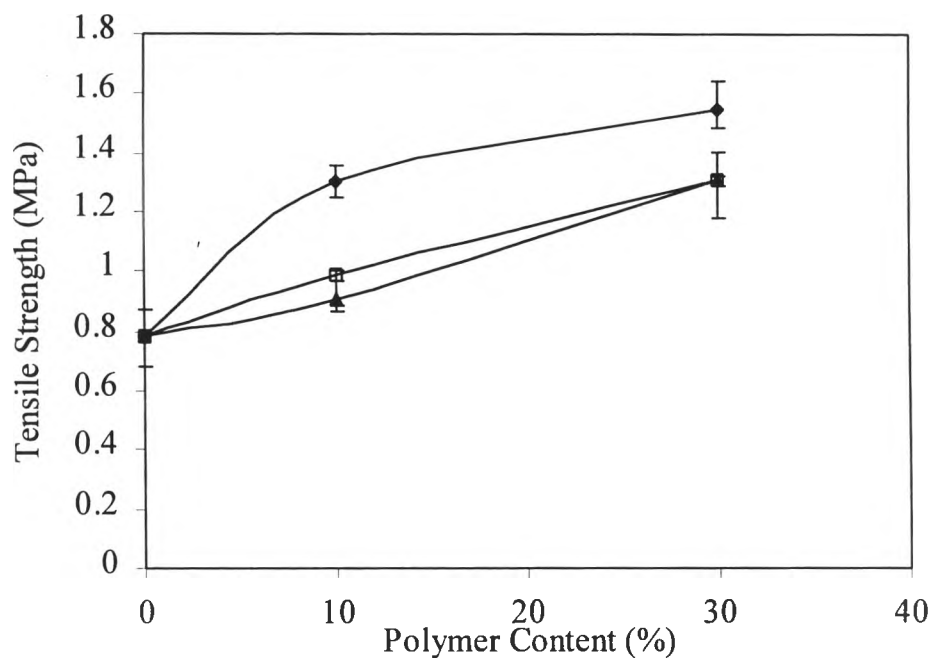


Figure 4.10 Tensile strength of starch-based composite foams at 42% RH for 2 days of (◆) starch-PVA foams, (□) starch-PLA foams, and (▲) starch-PCL foams.

Figure 4.10 shows the tensile strength of starch-based composite foams conditioned at 42% RH for 2 days as a function of polymer content. From this figure, the tensile strength increases with increasing polymer content. Tensile strength of starch, PVA, PLA, and, PCL are 22, 95, 44, and 33 MPa, respectively. In general, PVA, PLA, and PCL have greater tensile strength than starch so increasing the amounts of the polymers can improve tensile strength of starch foams. Similarly, Averous *et al.* (2000) found that the decreasing of PCL content led to the decreasing of tensile strength.

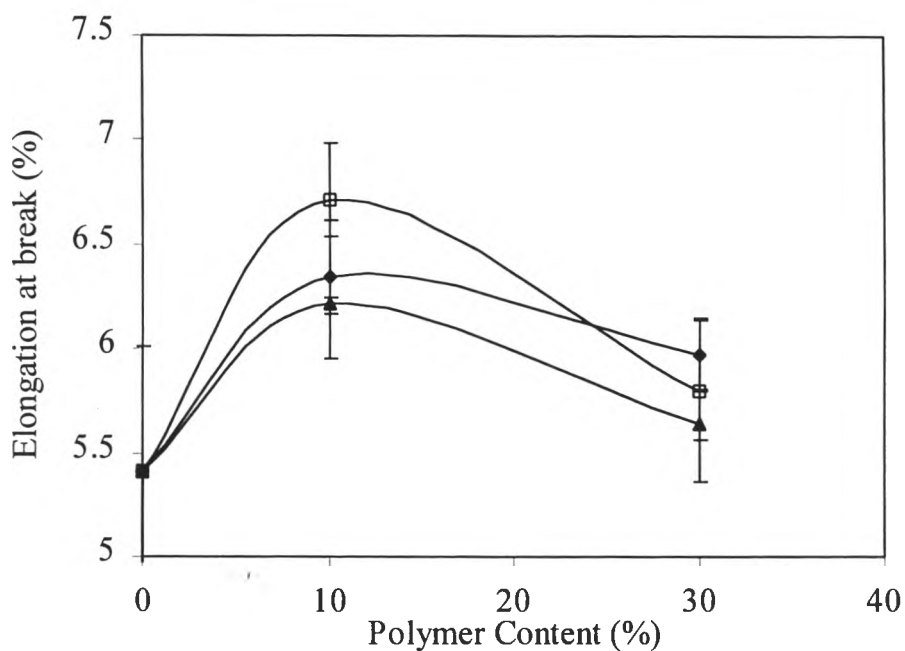


Figure 4.11 Elongation at break of starch-based composite foams at 42% RH for 2 days of (♦) starch-PVA foams, (□) starch-PLA foams, and (▲) starch-PCL foams.

Figure 4.11 shows elongation at break of starch-based composite foams conditioned at 42% RH for 2 days as a function of polymer content. Maximum elongation at break was found at 10% polymer content for all polymers. This may be due to the increasing of the hardness of starch-based composite foam by adding the polymers. Comparison between starch foam and foams containing synthetic biodegradable polymers, foams containing PVA, PLA, and PCL have greater elongation at break than starch foam. Similarly, Fang and Hanna (2000) reported that increasing the PLA content in starch-PLA foams made the foam more elastic.

4.3.1.4 Effect of Plasticizers on Tensile Properties

In most applications in which plasticizers are incorporated into plastics, their purpose is to convert an otherwise hard and rigid plastic to a flexible or semiflexible tough part. In this study, three plasticizers, which are glycerol, urea, and ammonium chloride, were added into starch foams in order to study their effects on tensile properties of the foams.

Tensile properties were measured after conditioning the foams at 25°C and 42% RH for 7 days. The results are plotted as a function of the amounts of plasticizers for the starch foams containing glycerol, urea, and ammonium chloride.

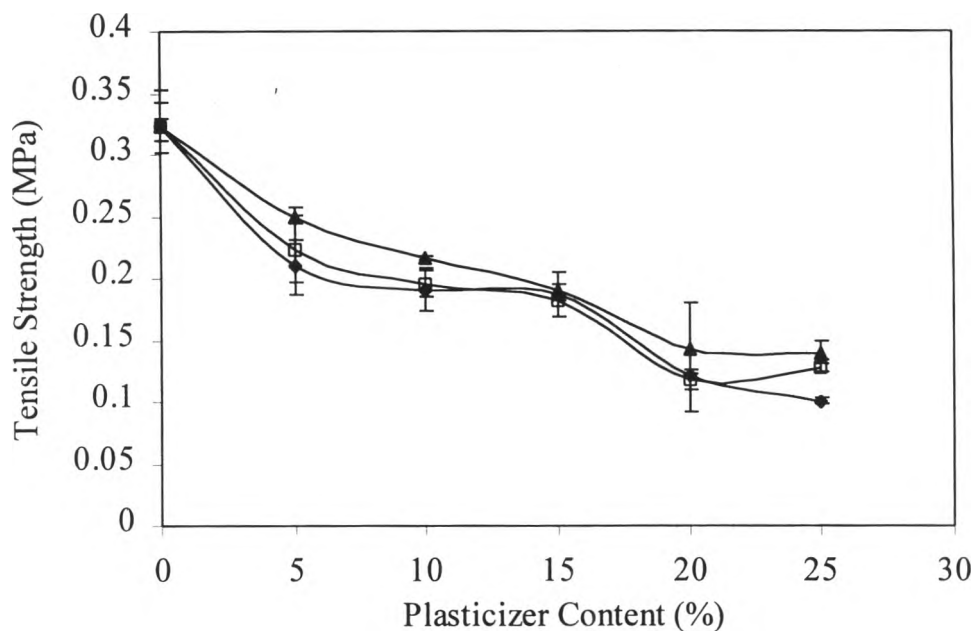


Figure 4.12 Effect of plasticizers on tensile strength of starch foams at 42% RH for 7 days of (◆) glycerol, (□) urea, and (▲) ammonium chloride.

In figure 4.12 it was found that the tensile strength decreases rapidly when the amounts of plasticizers increase. Because plasticizers can

penetrate into the starch granules and then destroy the inner hydrogen bonds of the starch. Jiugao *et al.* (1998) studied the properties of starch/glycerine blend and found that as a plasticizer, glycerine molecules could penetrate into the starch granules and then destroyed the inner hydrogen bonds of the starch. As a result, the binding force among starch macromolecule decreased that made tensile strength decreased. Stein and Greene (1997) used amino acids as plasticizers of starch plastics. They reported that as the concentration of plasticizers increased, tensile strength decreased.

Comparison between different types of plasticizers, it does not show much difference in decreasing tensile strength.

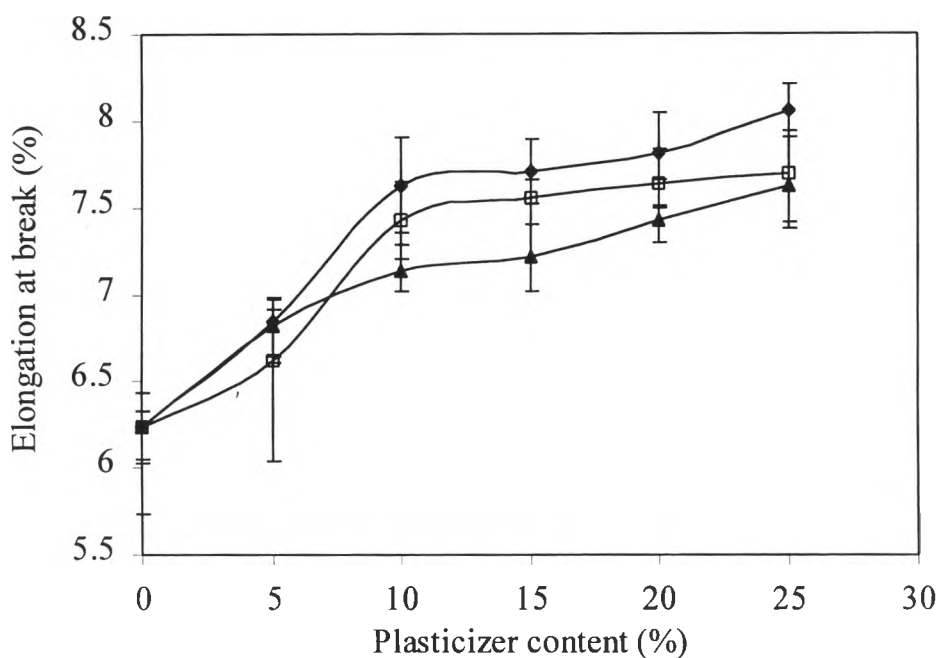


Figure 4.13 Effect of plasticizers on elongation at break of starch foams at 42% RH for 7 days of (◆) glycerol, (□) urea, and (▲) ammonium chloride.

The elongation at break as a function of plasticizer content is shown in figure 4.13. It was found that elongation at break increase with

increasing the plasticizer content. Generally, it is known that the addition of plasticizers can improve the elongation. The reason is that plasticizers destroy the inner hydrogen bonds of starch and then the binding force among macromolecules decreases, which makes it easy for molecular chains to slide (Jiugao *et al.*, 1998).

4.3.2 Flexural Properties

4.3.2.1 *Effect of Relative Humidity on Flexural Properties*

Flexural properties were measured after conditioning the foams at different relative humidity (11%, 32%, 42%, 52%, 67%, and 75% RH) at 25°C for 7 days. The results are plotted as a function of relative humidity for the starch-based composite foams containing different types of polymers (PVA, PLA, and PCL).

Flexural strength of starch-based composite foams containing PVA, PLA, and PCL as a functions of relative humidity are shown in figure 4.14. The flexural strength of the starch-based composite foams follows the same trend as the tensile strength (figure 4.6). This figure shows the maximum flexural strength at approximately 42% RH. For all formulations, at low humidities, brittleness and crack formation lead to lower strengths, while at high humidities, the plasticizing effects of large amounts of absorbed water lower the strength (Shogren, *et al.*, 1998a). In addition, increasing the polymer content makes the flexural strength increase.

Maximum strains or flexibilities of the starch-based composite foams as a function of relative humidity are shown in figure 4.15. It was found that increasing of relative humidities to 42% RH improved the maximum strain of foams. At relative humidity higher than 42% RH constant maximum strains were obtained. It may be due to the plasticizing effect of absorbed water at high humidities. Shogren *et al.* (1998b) found that maximum force of starch-PVA foams depended on relative humidity. At low and high humidities, foams showed low strength while 50% humidity, foams gave the maximum strength.

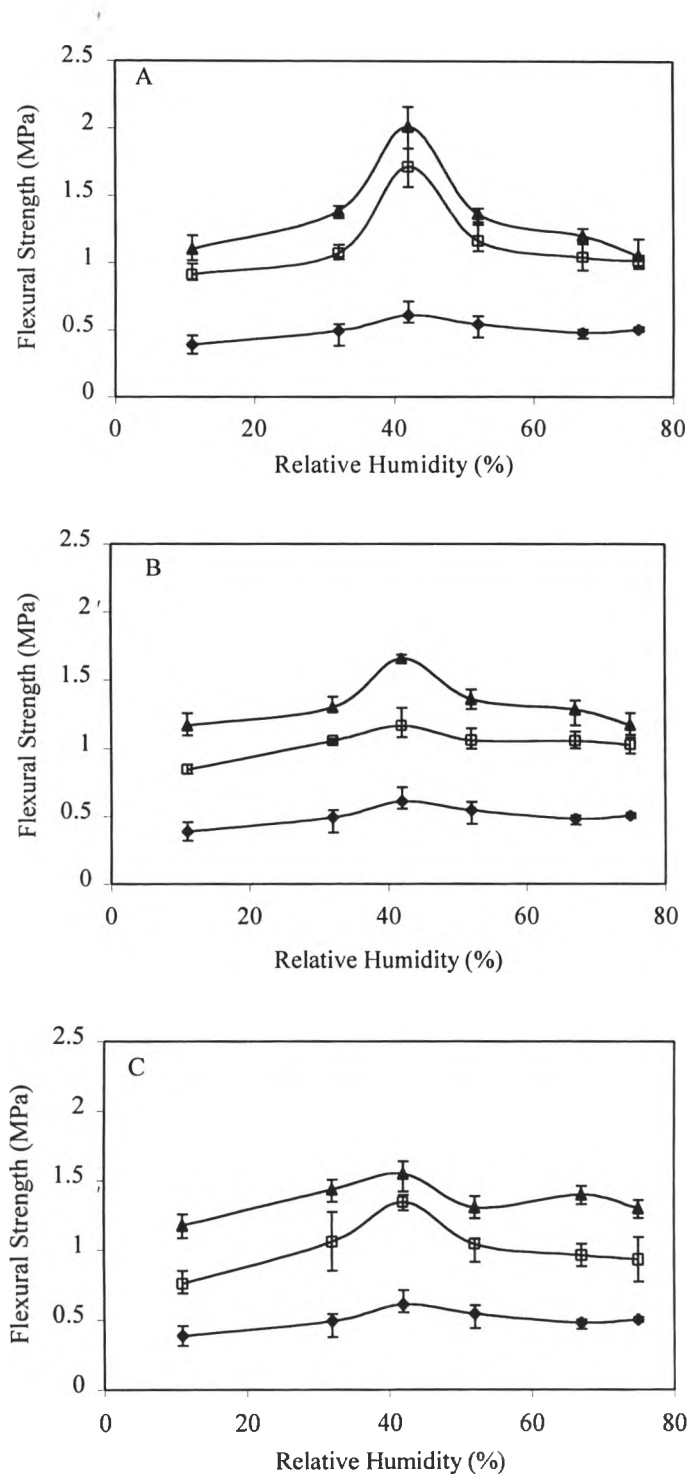


Figure 4.14 Flexural strength of starch-based composite foams as a function of relative humidity at 25°C for 7 days of (A) starch-PVA foams, (B) starch-PLA foams, and (C) starch-PCL foams: (◆) 0% synthetic polymer, (◻) 10% synthetic polymer, and (▲) 30% synthetic polymer.

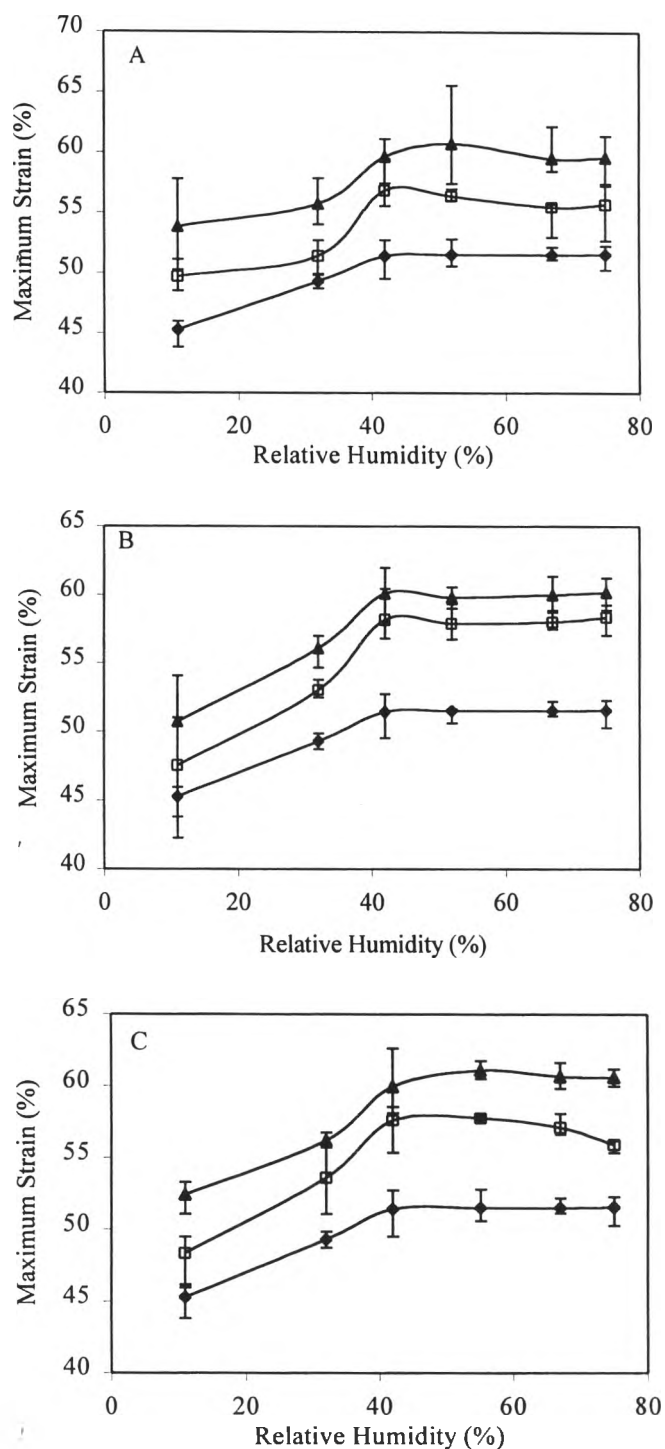


Figure 4.15 Maximum strain of starch-based composite foams as a function of relative humidity at 25°C for 7 days of (A) starch-PVA foams, (B) starch-PLA foams, and (C) starch-PCL foams: (♦) 0% synthetic polymer, (□) 10% synthetic polymer, and (▲) 30% synthetic polymer.

4.3.2.2 Effect of Storage Time on Flexural Properties

Flexural properties were measured after conditioning the foams at constant relative humidity of 42% RH at 25°C for several period of time. The results are plotted as a function of storage time for the starch-based composite foams containing different types of polymers (PVA, PLA, and PCL).

Flexural strengths of starch-based composite foams containing PVA, PLA, and PCL are shown in figure 4.16. The flexural strength of the starch-based composite foam follows the same trend as the tensile strength in figure 4.8. It should be noted that, the maximum flexural strengths are obtained at the second day of storage time for all formulations. It may be explained that increasing of moisture content in foams during storage could improve the mobility of the starch-based composite foams. In contrast, too high moisture content resulted in weakness of these foams. In addition, increasing of polymer content could improve flexural strength because PVA, PLA, and PCL are more flexible than starch (Shogren, *et al.*, 1998b; Avella, *et al.*, 2000; Fang and Hanna, 2000).

Maximum strains or flexibilities of the starch-based composite foams as a function of storage time are shown in figure 4.17. Maximum strain increases steadily for the first 4 days because of increased moisture content that is an increase of the number of water molecules surrounding the starch molecules to give more flexibility of starch-based composite foams. After 4 days, maximum strains of the foams become constant. Increasing of polymer content gave raise of the maximum strain of the composite foams over starch foam.

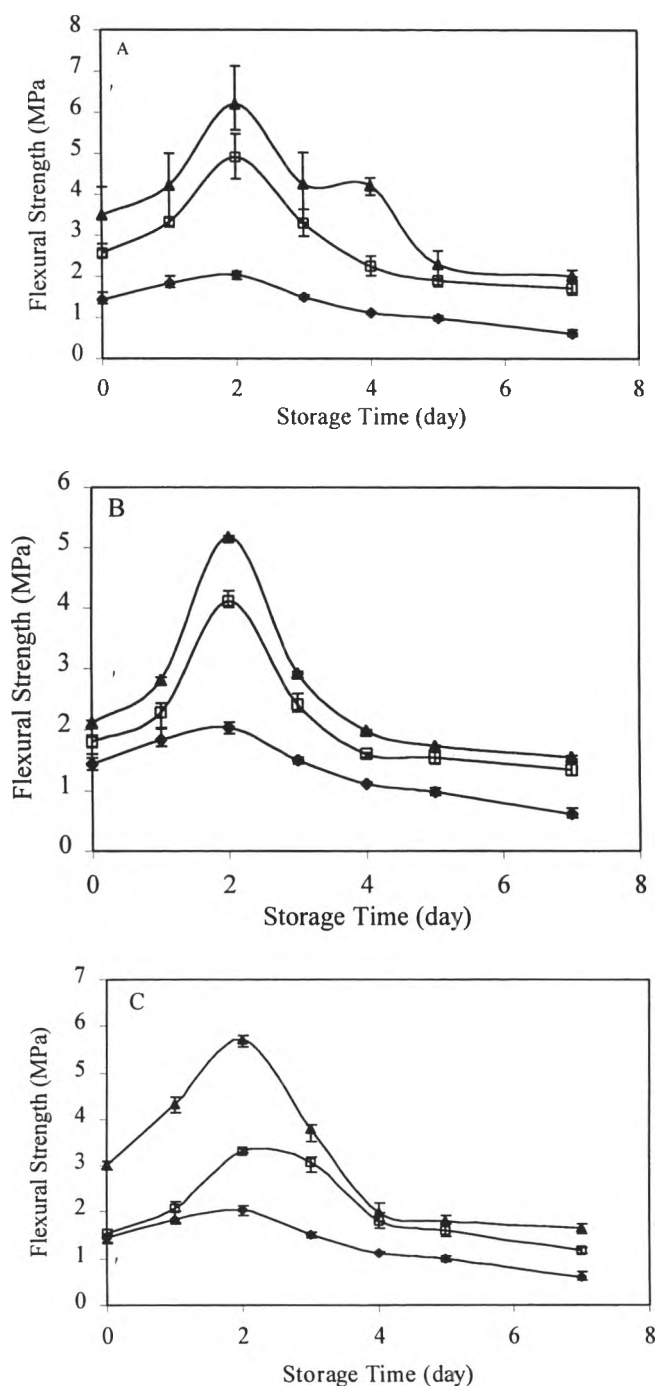


Figure 4.16 Flexural strength of starch-based composite foams as a function of storage time at 42% RH and 25°C of (A) starch-PVA foams, (B) starch-PLA foams, and (C) starch-PCL foams: (◆) 0% synthetic polymer, (□) 10% synthetic polymer, and (▲) 30% synthetic polymer.

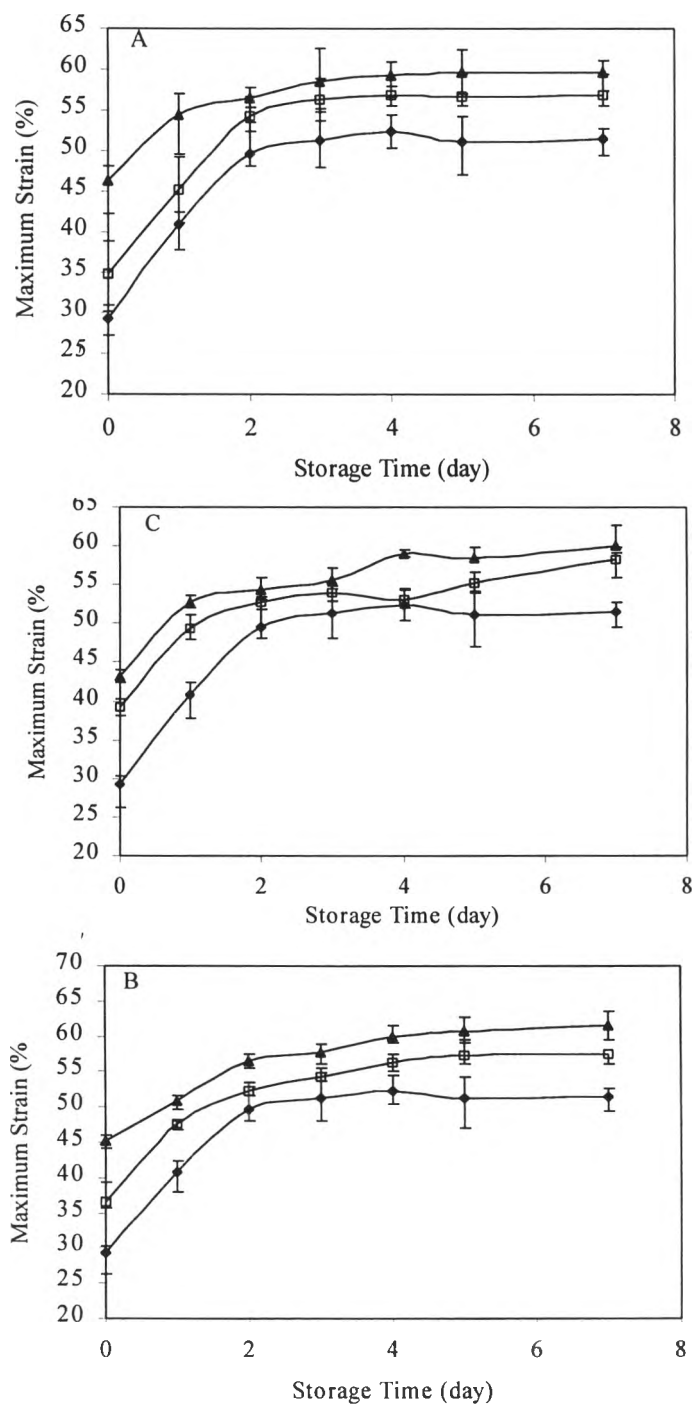


Figure 4.17 Maximum strain of starch-based composite foams as a function of storage time at 42% RH and 25°C of (A) starch-PVA foams, (B) starch-PLA foams, and (C) starch-PCL foams: (◆) 0% synthetic polymer, (□) 10% synthetic polymer, and (▲) 30% synthetic polymer.

4.3.2.3 Effect of Polymer on Flexural Properties

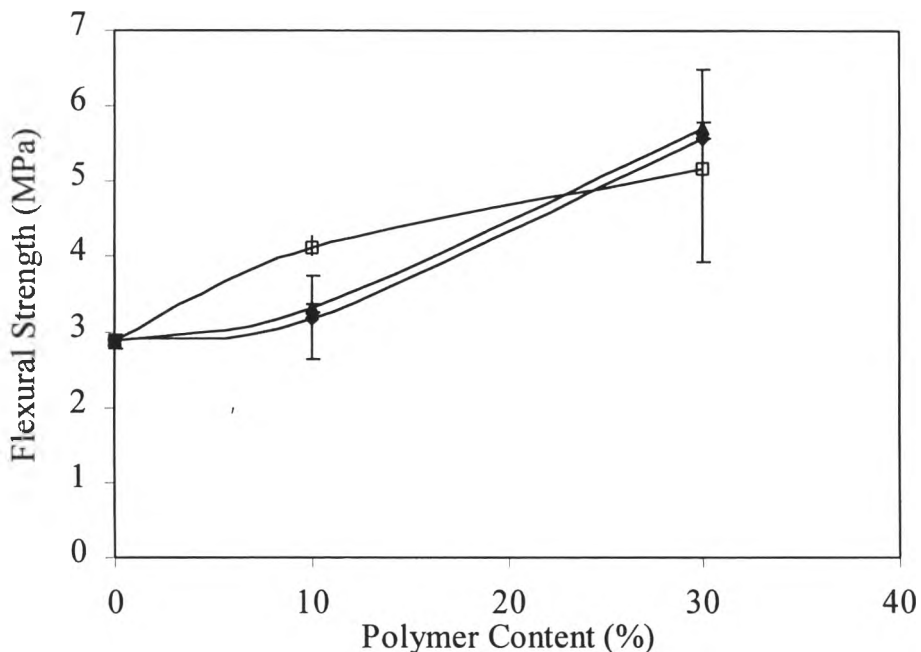


Figure 4.18 Flexural strength of starch-based composite foams at 42% RH for 2 days of (◆) starch-PVA foams, (□) starch-PLA foams, and (▲) starch-PCL foams.

Figure 4.18 shows the effect of polymer content on flexural strength of starch-based composite foams conditioned at 42% RH for 2 days. It was found that flexural strength of the foams increases with increasing polymer content. In general, PVA, PLA, and PCL have higher tensile strength than starch so increasing the amount of polymers could improve tensile strength of the foams.(Chang-Hyeon, 1999; Averous, 2000; Fang and Hanna, 2000).

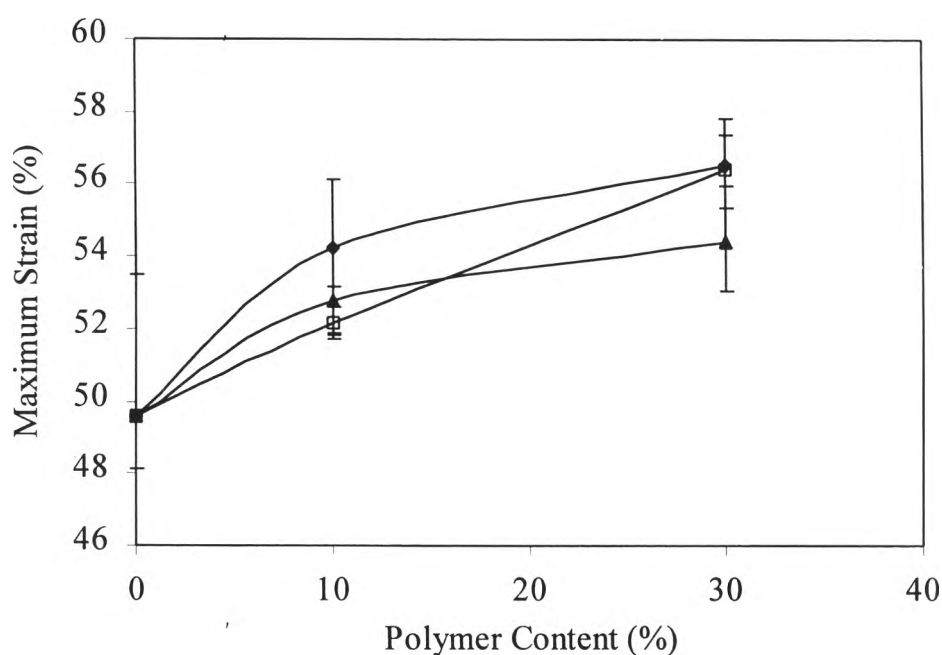


Figure 4.19 Maximum strain of starch-based composite foams at 42% RH for 2 days of (♦) starch-PVA foams, (□) starch-PLA foams, and (▲) starch-PCL foams.

Figure 4.19 shows the effect of polymer content on maximum strain of starch-based composite foams conditioned at 42% RH for 2 days. It was found that maximum strain increases with increasing of polymer content. Comparison between starch foam and foams containing synthetic biodegradable polymers, foams containing PVA, PLA, and PCL have greater maximum strain than starch foam. Similarly, Fang and Hanna (2000) reported that increasing the PLA content in starch-PLA foams made the foam more elastic.

4.3.2.4 Effect of plasticizers content on flexural properties

Flexural properties were measured after conditioning the foams at 25°C and 42% RH for 7 days. The results are plotted as a function plasticizer content for the starch foams containing different types of plasticizers (glycerol, urea, and ammonium chloride).

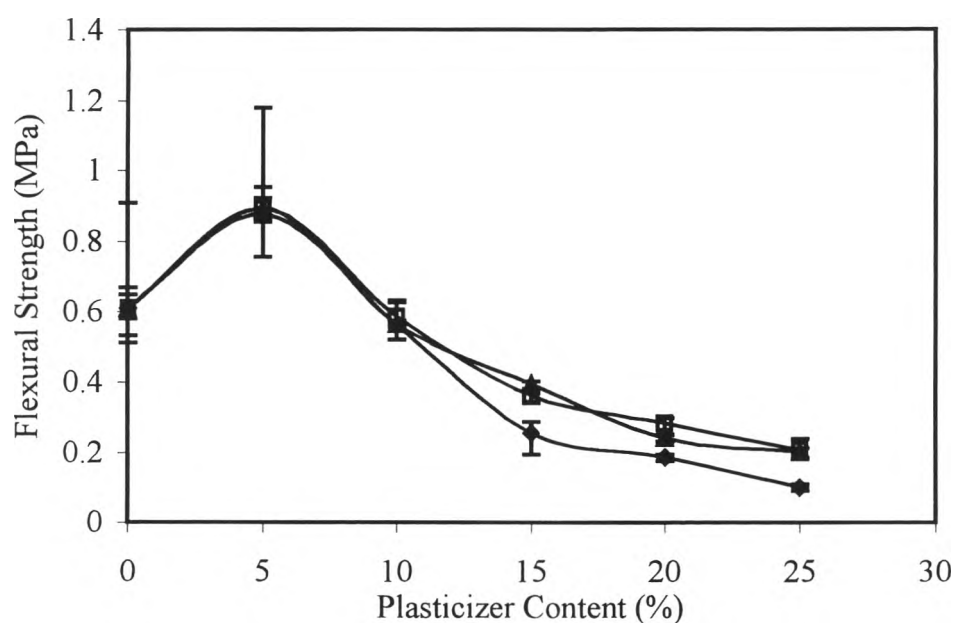


Figure 4.20 Effect of plasticizers on flexural strength of starch foams at 42% RH for 7 days of (◆) glycerol, (□) urea, and (▲) ammonium chloride.

Flexural strength of starch foams containing three different plasticizers is shown in figure 4.20. The maximum flexural strength is found for the foam containing 5% plasticizers. For the foams containing more than 5% plasticizers, the flexural strength decrease rapidly because plasticizers destroy the binding force among starch macromolecules (Jiugao *et al.*, 1998).

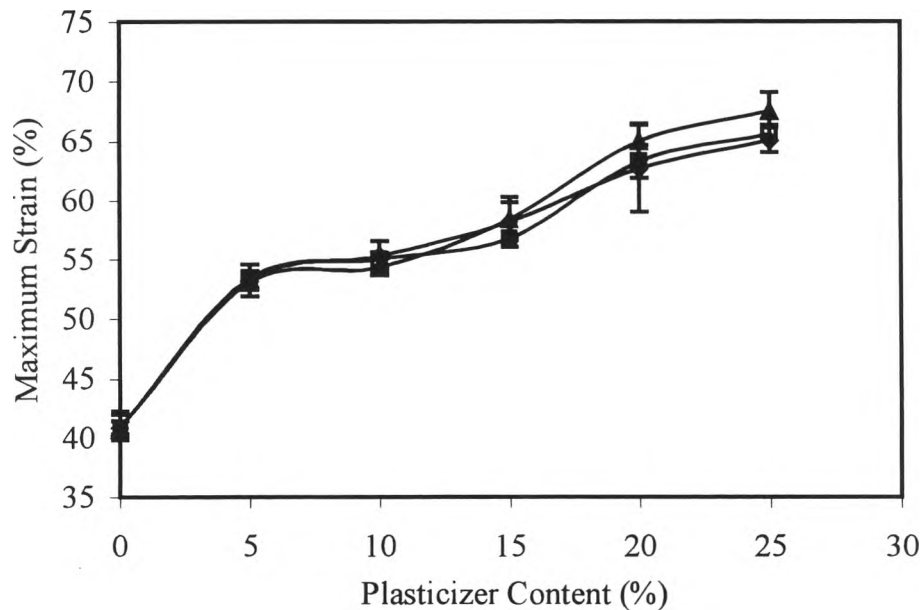


Figure 4.21 Effect of plasticizers on maximum strain of starch foams at 42% RH for 7 days of (◆) glycerol, (□) urea, and (▲) ammonium chloride.

The effect of plasticizer content on the maximum strain is shown in figure 4.21. The maximum strain rises steeply with the increasing of plasticizers content. Because plasticizers destroy the inner hydrogen bonds of starch and then the binding force among starch macromolecules decreases, which makes it easy for molecular chains to slide (Jiugao *et al.*, 1998). Van Soest and Knooren (1997) found that increasing glycerol led to decreasing strength of extruded starch plastic sheets. Comparison between types of plasticizers, it does not show much different in decreasing of tensile strength and increasing of maximum strain.

4.4 Water Absorption

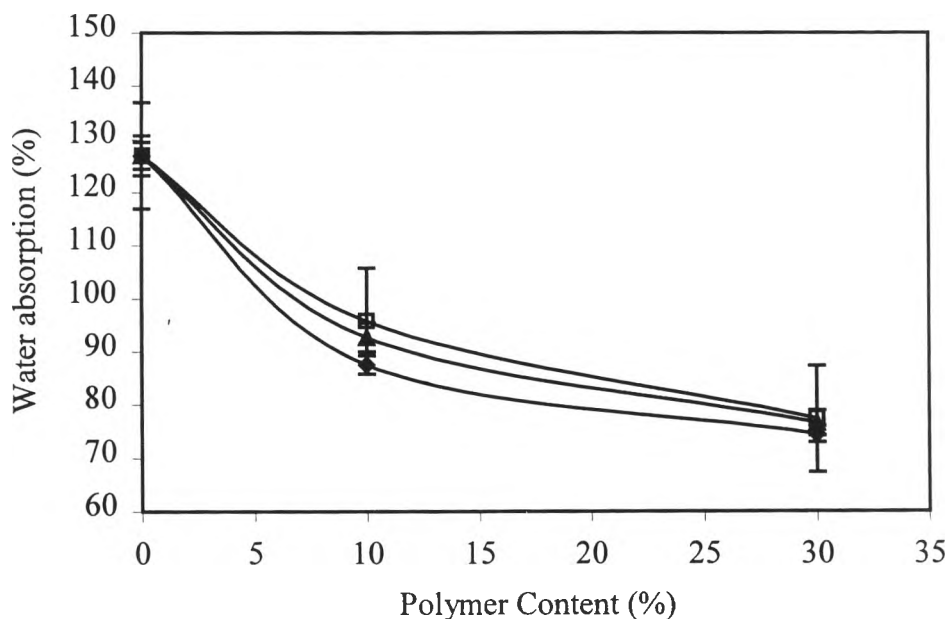


Figure 4.22 Water absorption of starch-based composite foams of (◆) starch-PVA foams, (□) starch-PLA foams, and (▲) starch-PCL foams.

The water absorption of starch-based composite foams containing PVA, PLA, and PCL as a function of polymer content is shown in figure 4.22. Water absorption decreases with the increasing of polymer content. Similarly, Shogren *et al.* (1998) reported that water absorption decreased with increasing 98% hydrolyzed PVA content. This is because 98% hydrolysed PVA is highly crystalline and cold-water-insoluble. Fang and Hanna (2000) found that water solubility index of starch-PLA foams decreased with increasing PLA.

4.5 Enzymatic Degradation

Enzyme α -amylase was used to examine the degradation of starch component in the starch-based composite foams containing PVA, PLA, and PCL. The advantages of the enzymatic biodegradation tests are that they are usually easy to perform, the results can be achieved very rapidly, and degradation products can be analyzed qualitatively without interference from microbial growth or metabolic products (Allenza, 1990).

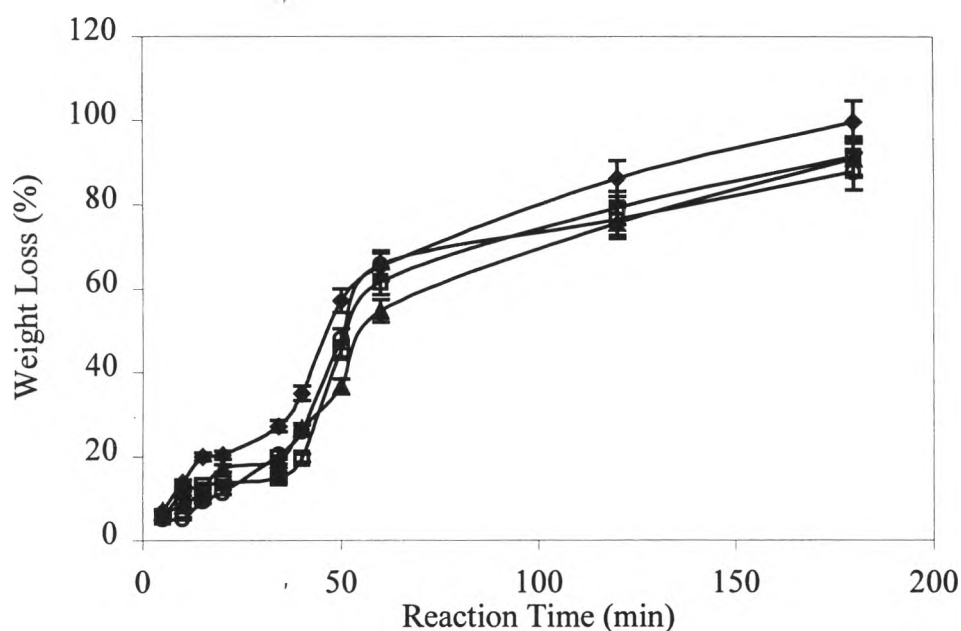


Figure 4.23 Enzymatic degradation of starch-based composite foams by α -amylase at 55°C of (◆) starch foam, (□) starch-30% PVA foams, (▲) starch-30% PLA foams, and (○) starch-30% PCL.

The biodegradability of the starch-based composite foams by enzymatic hydrolysis is shown in figure 4.23. The weight loss of all starch-based composite foams increased with increasing reaction time and the foams containing synthetic biodegradable polymers showed slightly different weight loss of the starch only. These results indicate that the synthetic biodegradable

polymer in starch-based composite foams was slightly influence of degradation of starch. Vikman *et al.* (1999) found that enzymatic hydrolysis of the milled thermoplastic starch (TPS)-PCL samples was more rapid as compared to the TPS-PCL pieces, indicating the importance of surface area of the sample in the biodegradation tests. The PCL layer on the surface of the TPS-PCL plates reduced the rate of the enzymatic hydrolysis.